

# PATENT SPECIFICATION

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## PROVISIONAL SPECIFICATION.

### Improvements relating to the Preparation of Catalysts.

We, ANGLO-IRANIAN OIL COMPANY LIMITED, of Britannic House, Finsbury Circus, London, E.C.2, a British joint-stock Corporation, JACK OWEN, LESLIE CHRISTOPHER STRANG and JOHN NORMAN HARESNAPE, all of Research Station, Anglo-Iranian Oil Company Limited, Chertsey Road, Sunbury-on-Thames, Middlesex, all of British Nationality, do hereby declare the nature of this invention to be as follows:—

This invention relates to the preparation of catalysts for use in hydrogenation reactions and more particularly to the preparation of catalysts of the cobalt molybdate type.

It is known that a catalyst of the cobalt molybdate type, particularly when the cobalt molybdate is deposited on or incorporated with a material such as alumina, is a particularly effective catalyst for use in such reactions as the hydrogenation of unsaturated hydrocarbons and the desulphurisation of petroleum hydrocarbons by the hydrofining process.

In known methods of preparing the catalyst involving co-precipitation of alumina gel and cobalt molybdate, the alumina gel being derived from a solution of an aluminium salt, it is necessary to use a relatively expensive aluminium salt such as the chloride or nitrate, instead of the cheaper sulphate, if contamination of the catalyst by acid radicals (which cannot be removed by heat) is to be avoided. The extensive washing of such a catalyst after precipitation is not practicable without considerable losses of cobalt molybdate.

The invention has among its objects to prepare a cobalt molybdate catalyst of high activity without the use of specially prepared alumina, so that any commercially available porous alumina may be used in the preparation of the catalyst.

According to the invention, a cobalt molybdate catalyst is prepared by mixing an aqueous solution of a cobalt salt with an aqueous solution of a salt of molybdic acid in the presence of ammonia, thereby precipitating cobalt molybdate, adding more ammonia to re-dissolve the precipitate, mixing the resulting solution with anhydrous, porous gamma alumina so that the solution is absorbed wholly or in part by the porous alumina, and evaporating to dryness.

Cobalt nitrate is the preferred cobalt salt and ammonium molybdate the preferred salt of molybdic acid, as by their use, the contamination of the catalyst by radicals which cannot be driven off by heating, is avoided.

An example of the process according to the invention will now be described.

#### EXAMPLE.

Alumina granules of the type sold commercially as a drying agent and consisting largely of boehmite,  $Al_2O_3 \cdot H_2O$ , were roasted for two hours at  $1020^\circ F.$ , and as a result all the water was driven off and anhydrous gamma alumina,  $Al_2O_3$ , remained. 320 gm. of ammonium molybdate  $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$  were dissolved in 400 ml. of distilled water and 400 ml. of aqueous ammonia (s.g. 0.880), and 263 gm. of cobalt nitrate  $Co(NO_3)_2 \cdot 6H_2O$  were dissolved in 400 ml. of distilled water. The two solutions were mixed and the precipitate which formed was dissolved by adding 2000 ml. of 0.880 ammonia. The hot solution was added to 2000 gm. of the alumina heated to  $212^\circ F.$ , in a metal tray. The supernatant liquid was drained off, the impregnated alumina dried and re-impregnated with the aqueous solution and once more dried. The catalyst was given a final heat treatment for two hours at  $1020^\circ F.$ , and was then ready for use.

Dated the 30th day of January, 1948.

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## COMPLETE SPECIFICATION

## Improvements relating to the Preparation of Catalysts.

We, ANGLO-IRANIAN OIL COMPANY LIMITED, of Britannic House, Finsbury Circus, London, E.C.2, a British joint-stock Corporation, JACK OWEN, LESLIE CHRISTOPHER STRANG and JOHN NORMAN HARESHAPE, all of Research Station, Anglo-Iranian Oil Company Limited, Chertsey Road, Sunbury-on-Thames, Middlesex, all of British Nationality, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the preparation of catalysts for use in hydrogenation reactions and more particularly to the preparation of catalysts of the cobalt molybdate type.

It is known that a catalyst of the cobalt molybdate type, particularly when the cobalt molybdate is deposited on or incorporated with a material such as alumina, is a particularly effective catalyst for use in such reactions as the hydrogenation of unsaturated hydrocarbons and the desulphurisation of petroleum hydrocarbons by the hydrofining process.

In known methods of preparing the catalyst involving co-precipitation of alumina gel and cobalt molybdate, the alumina gel being derived from a solution of an aluminium salt, it is necessary to use a relatively expensive aluminium salt such as the chloride or nitrate, instead of the cheaper sulphate, if contamination of the catalyst by acid radicals (which cannot be removed by heat) is to be avoided. The extensive washing of such a catalyst after precipitation is not practicable without considerable losses of cobalt molybdate.

The invention has among its objects to prepare a cobalt molybdate catalyst of high activity without the use of specially prepared alumina, so that any commercially available porous alumina may be used in the preparation of the catalyst.

According to the invention, a cobalt molybdate catalyst is prepared by reacting a cobalt salt and a salt of molybdic acid in aqueous ammoniacal solution so as to form a solution of a cobalt molybdate-ammonia complex, mixing the solution with a support selected from the class consisting of anhydrous porous gamma alumina and mixtures of boehmite and gamma alumina prepared by partially dehydrating boehmite, so that the solution is absorbed wholly or in part by the support, evaporating to dryness and heating the impregnated support at an elevated tem-

perature above 1000°F., to convert the complex into the desired catalytic form.

The solution of the cobalt molybdate-ammonia complex may be prepared by mixing an aqueous solution of a cobalt salt with an aqueous solution of a salt of molybdic acid in the presence of ammonia so as to precipitate cobalt molybdate, and adding more ammonia to re-dissolve the precipitate.

Alternatively, the solution of the cobalt molybdate-ammonia complex may be prepared without the intermediate formation of the cobalt molybdate precipitate by using a sufficient excess of ammonia in the solution of the salt of molybdic acid.

In order to avoid the formation of cobalt hydroxide, ammonia should not be introduced into the solution of the cobalt salt prior to its being mixed with the solution of the salt of molybdic acid.

Cobalt nitrate is the preferred cobalt salt and ammonium molybdate the preferred salt of molybdic acid, as by their use, the contamination of the catalyst by radicals which cannot be driven off by heating, is avoided.

Two examples of the process according to the invention will now be described, the second with reference to the accompanying diagrammatic drawing.

## EXAMPLE I.

Alumina granules of the type sold commercially as a drying agent and consisting largely of boehmite,  $Al_2O_3 \cdot H_2O$ , were roasted for two hours at 1020°F., and as a result all the water was driven off and anhydrous gamma alumina,  $Al_2O_3$ , remained. 320 gm. of ammonium molybdate  $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$  were dissolved in 400 ml. of distilled water and 400 ml. of aqueous ammonia (s.g. 0.880), and 263 gm. of cobalt nitrate  $Co(NO_3)_2 \cdot 6H_2O$  were dissolved in 400 ml. of distilled water. The two solutions were mixed and the precipitate which formed was dissolved by adding 2000 ml. of 0.800 ammonia. The hot solution was added to 2000 gm. of the alumina heated to 212°F., in a metal tray. The supernatant liquid was drained off, the impregnated alumina dried and re-impregnated with the aqueous solution and once more dried. The catalyst was given a final heat treatment for two hours at 1020°F., and was then ready for use.

## EXAMPLE II.

70 lb. of alumina granules of nominal 2-4 mesh size, previously activated by heating, and consisting of boehmite,  $Al_2O_3 \cdot H_2O$  and anhydrous gamma alumina, were charged to a cylindrical steel vessel fitted with an inlet

11 and an outlet 12 for solids, and adapted to be electrically heated. Absorbed moisture was removed by blowing air at 120°C., (as indicated by a thermocouple in an axial thermocouple well 13), and the vessel 10 was then cooled to 60°C., and held at that temperature.

18 gallons of a solution containing 10.7% wt. of molybdenum, 2.9% wt. of cobalt, and 9.25% wt. of ammonia (NH<sub>3</sub>) was made up using ammonium molybdate, cobalt nitrate and aqueous ammonia in the manner detailed in Example I. This solution was placed in the vessel 14 which is adapted to be steam-heated. All outlets from the vessel to the atmosphere were closed, to prevent loss of ammonia vapour, and the temperature of the solution was raised to 60°C. The solution was then circulated upwardly at this temperature through the alumina in the vessel 10 by means of the pump 15, the solution returning to the vessel 14 via the line 16. After 4 hours, the circulation of the solution was stopped, surplus solution was allowed to drain from the vessel 10 into the vessel 14, and the impregnated alumina then dried by blowing air at 120-150°C., upwardly through the vessel 10, which was also slowly heated externally and vented at 17. When the temperature, as indicated by the thermocouple in the well 13, rose to 120°C., the air was shut off and the heating continued with the vent 17 open, until a temperature of 550°C., was reached, at which temperature level the heating was continued for a further 3 hours. The catalyst so prepared was cooled and was then ready for use. The surplus solution in vessel 14 was made up to its original strength and volume by adding suitable amounts of chemicals, and was again used on a fresh charge of alumina.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of preparing a cobalt molybdate catalyst, which comprises reacting a cobalt salt and a salt of molybdic acid in aqueous ammoniacal solution so as to form a solution of a cobalt molybdate-ammonia complex, mixing the solution with a support

selected from the class consisting of anhydrous porous gamma alumina and mixtures of boehmite and gamma alumina prepared by partially dehydrating boehmite, so that the solution is absorbed wholly or in part by the support, evaporating to dryness, and heating the impregnated support at an elevated temperature above 1000°F., to convert the complex into the desired catalytic form.

2. A method according to Claim 1, in which the solution of the cobalt molybdate-ammonia complex is prepared by mixing an aqueous solution of a cobalt salt with an aqueous solution of a salt of molybdic acid in the presence of ammonia so as to precipitate cobalt molybdate and adding more ammonia to redissolve the precipitate.

3. A method according to Claim 1, in which the solution of the cobalt molybdate-ammonia complex is prepared by mixing an aqueous solution of a cobalt salt with an aqueous solution of a salt of molybdic acid in the presence of an excess of ammonia.

4. A method of preparing a cobalt molybdate catalyst as claimed in any of Claims 1-3, in which the cobalt salt is cobalt nitrate.

5. A method of preparing a cobalt molybdate catalyst as claimed in any of Claims 1-4 in which the salt of molybdic acid is ammonium molybdate.

6. A method according to any of the preceding Claims, in which the cobalt molybdate-ammonia complex solution is hot when mixed with the support which has been heated, the supernatant liquid being drained off prior to the drying and the heating of the impregnated support.

7. A method of preparing a cobalt molybdate catalyst as claimed in Claim 6, in which the dried impregnated support is re-impregnated with the supernatant liquid and again dried and finally heated.

8. A method of preparing a cobalt molybdate catalyst as described in Example I.

9. A method of preparing a cobalt molybdate catalyst as described in Example II.

Dated this 26th day of January, 1949.

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[This Drawing is a reproduction of the Original on a reduced scale.]

